Use of Organic Substrates as a Best Management Practice for Active Ranges

Robert C. Borden, Bilgen Yuncu, Stewart Farling
North Carolina State University

Tony Lieberman, Ed Alperin
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14. ABSTRACT

Ongoing use of firing ranges and open burn/open detonation area can result in accumulation of high explosive (HE) and propellant residues that can be transported to groundwater in high permeability soils. However, leaching is much more limited in high organic carbon soils due to a combination of enhanced sorption and degradation. Organic materials can enhance explosive degradation by stimulating anaerobic biodegradation of the target contaminants and reducing naturally occurring Fe(III) to Fe(II), providing a reservoir of reducing power to maintain anoxic conditions in the soil and enhance abiotic degradation. Humic materials slowly biodegrade, consuming oxygen, enhancing hydrophobic sorption and covalent binding, and may potentially serve as electron shuttles, enhancing abiotic degradation by Fe(II). ESTCP Project ?Generation of Biodegradation-Sorption Barriers for Munitions Constituents? (ER-201123) is developing a process to reduce leaching of explosives and propellants by spray application of an amendment solution containing a soluble, easily biodegradable organic substrate and a soluble humic material on the soil surface, followed by irrigation to carry the amendments deeper into the soil profile. Irrigation and transport of the amendments into the soil profile will reduce fire hazards, generate more strongly reducing conditions, and increase treatment longevity.

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ORGANIC SUBSTRATE ADDITION AS A RANGE BEST MANAGEMENT PRACTICE

DR. ROBERT C. BORDEN
North Carolina State University
Campus Box 7908
Raleigh, NC 27695
(919) 515-1625
rcborden@eos.ncsu.edu

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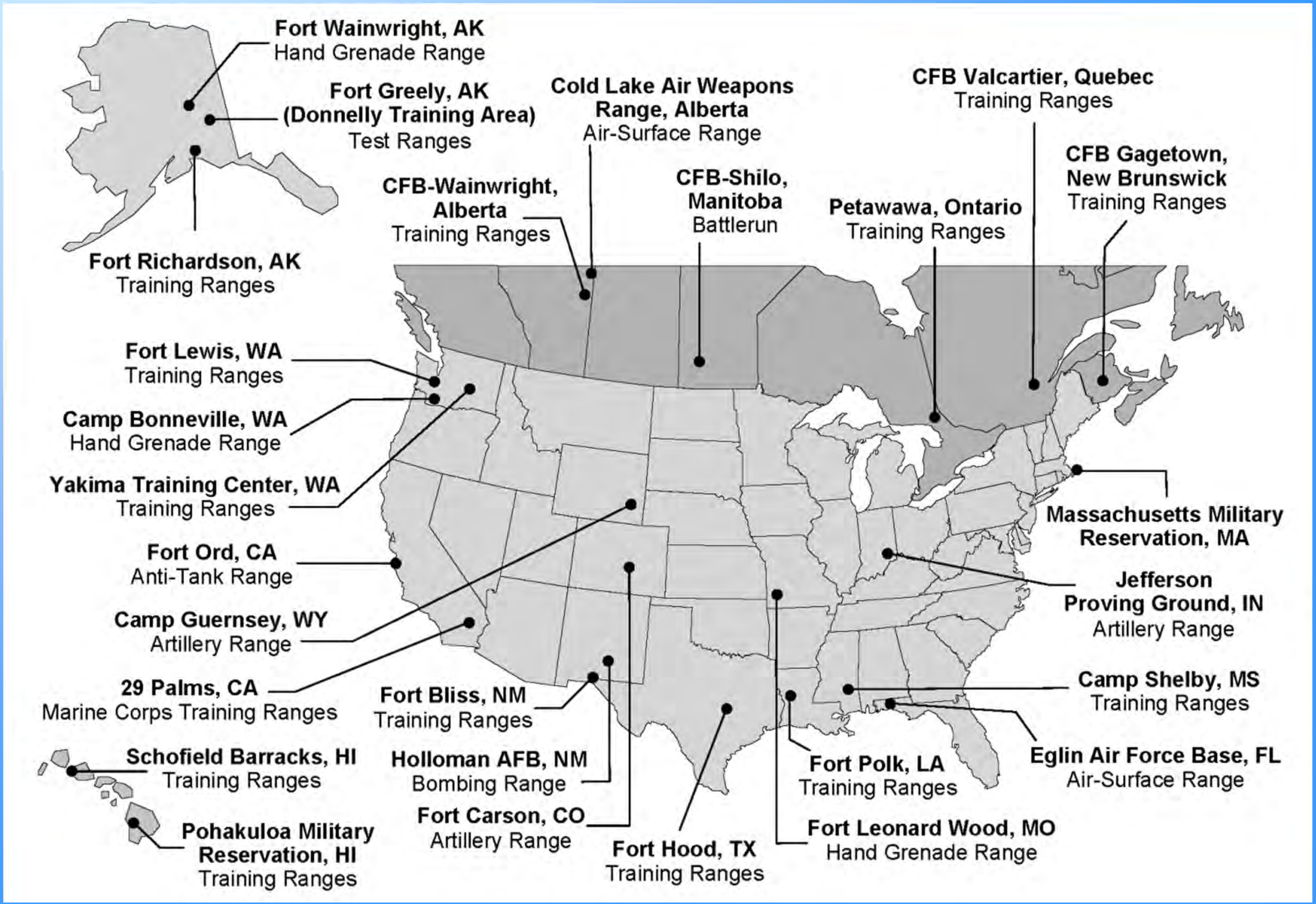
Explosives and Propellants Deposition on Ranges

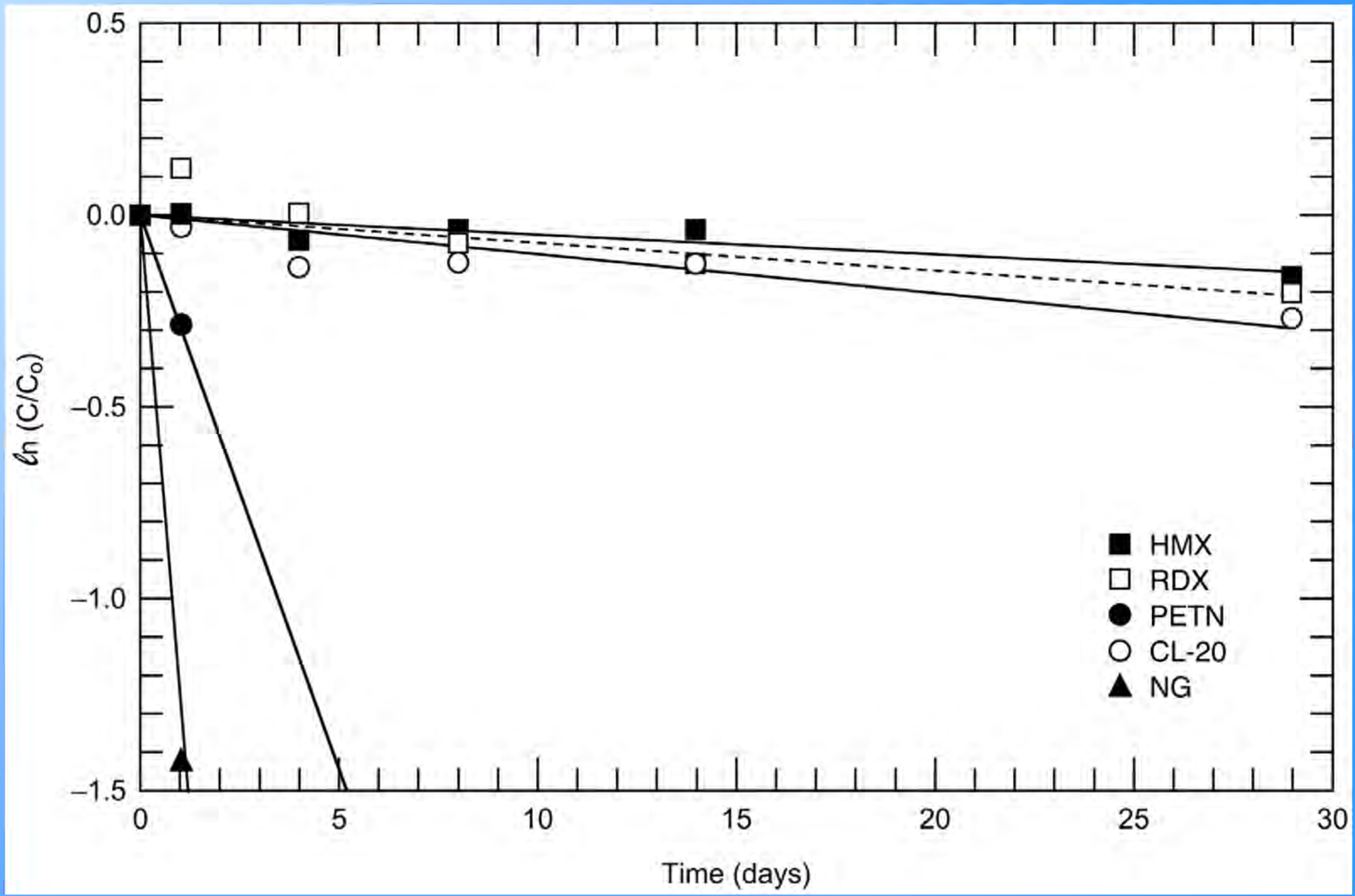


E&P Properties

Property	Drinking Water Limit (mg/L)	Aqueous Solubility (mg/L)	Sorption to Soil	Biodegradation	
				Aerobic	Anaerobic
Nitrocellulose (NC)	Nontoxic	Insoluble	NA	Low	Low
Nitroglycerin (NG)	5	~1,400	Low	High	High
Dinitrotoluene (DNT)	0.110	180-270	High	High	Moderate
Trinitrotoluene (TNT)	0.002	~130	High	Moderate	High
High Melting Explosive (HMX)	0.400	7-8	Low	Low	Moderate
Royal Demolition Explosive (RDX)	0.002	42	Low	Low	Moderate
Perchlorate (AP)	0.015	> 15,000	Low	Low	High

Explosive Loss in Fort Greely Soil

- **Unsaturated, aerobic sand**
- **NG rapidly degraded**
- **Minimal loss of HMX or RDX**



Jenkins, Bartolini, and Ranney, 2003. Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil, ERDC/CRREL TR-03-7

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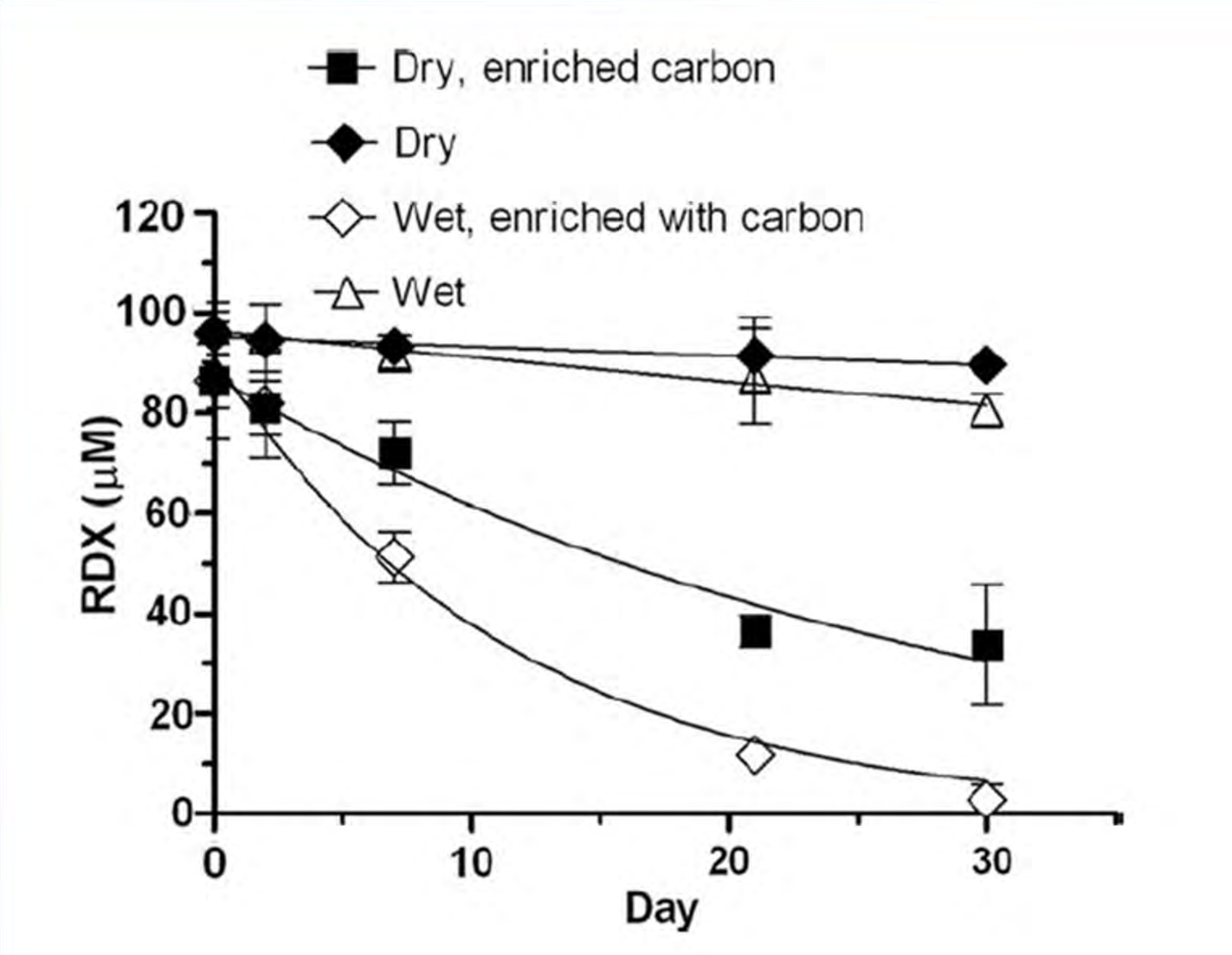
RDX Biodegradation in Microcosms

- Shallow (50 cm) deep soil
- Carbon addition accelerates degradation
- Rates are higher for moist soil



Ronen, Yanovich, Goldin, and Adar, 2008. Metabolism of the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in a contaminated vadose zone, Chemosphere.

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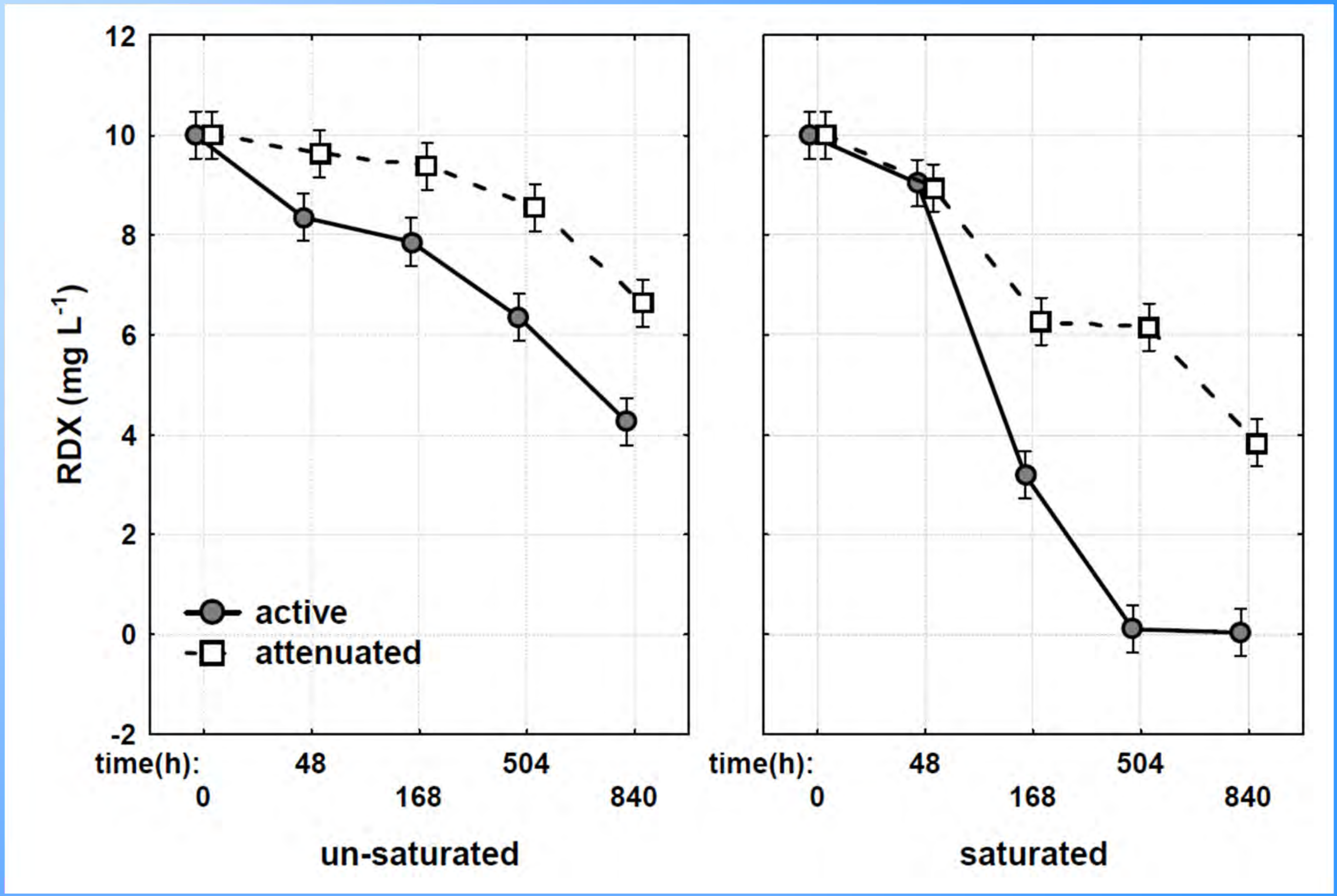
Effect of Soil Water on RDX Biodegradation

- Soil
  - 10.4 % organic matter
  - 58% sand, 35% silt, 7% clay
- Un-saturated soil
  - remained aerobic
  - ~50% RDX loss over 35 d
- Saturated soil
  - Anaerobic
  - RDX is BDL after 21 days



Ringelberg, Reynolds, Foley, and Perry, 2005. Microbial Community Shifts Associated with RDX Loss in a Saturated and Well-Drained Surface Soil, ERDC/CRREL TR-05-4

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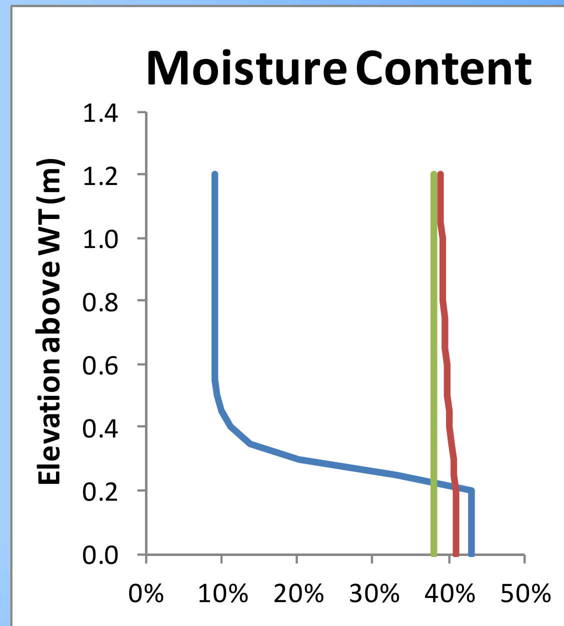
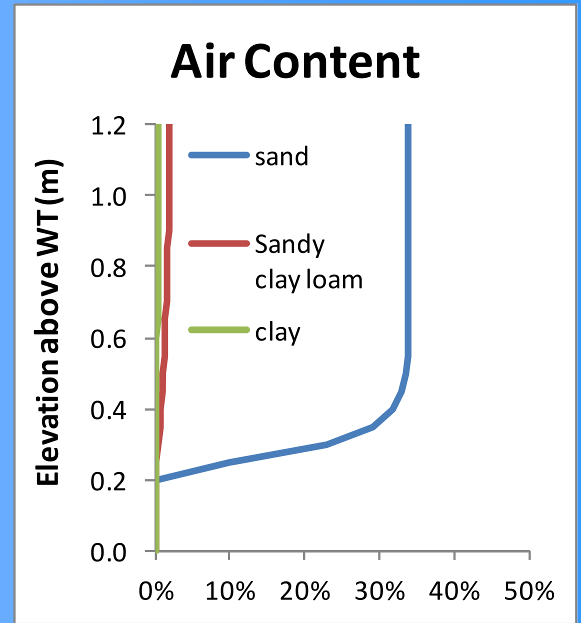
RDX Biodegradation

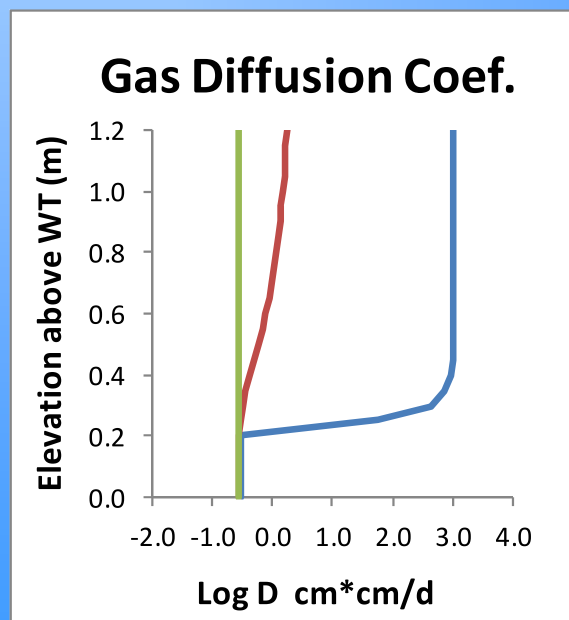
- Aerobic conditions
  - low/zero degradation
  - Potential GW contamination
- Anaerobic Conditions
  - rapid degradation
  - No GW contamination
- Conclusion
  - Make soil anaerobic
  - How?

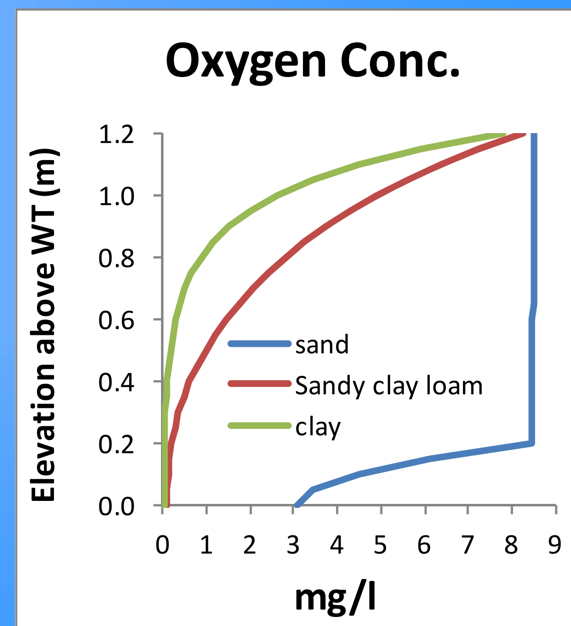
Oxygen (O_2) Status of Natural Soils

- O_2 consumption by organic matter
- O_2 transport
  - Primarily diffusion
  - $D_{gas} >> D_{water}$
  - Primary control is air filled pores
- Water retention
  - Low in sand
  - High in clay
- O_2 transport
  - High in sand
  - Low in clay









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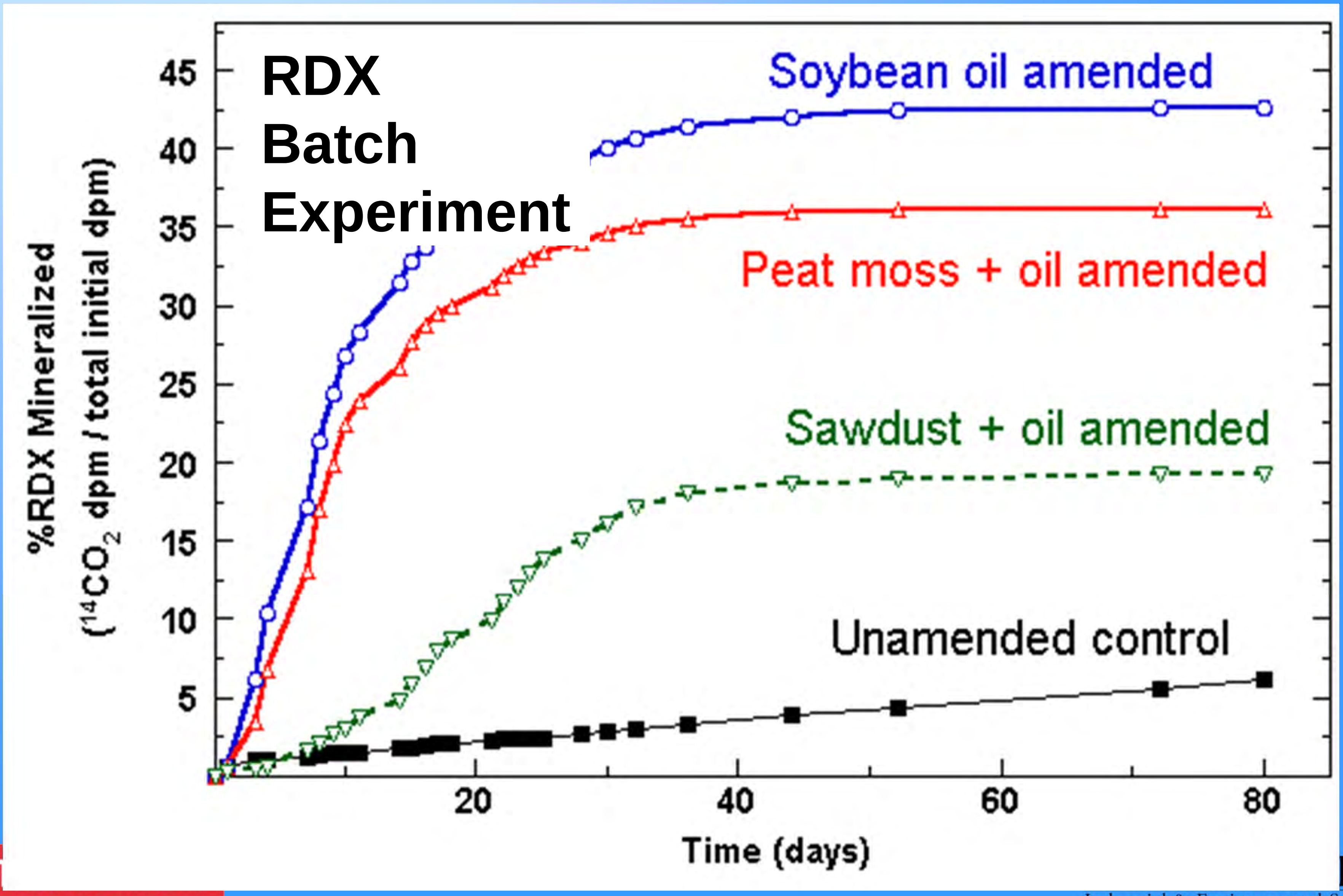
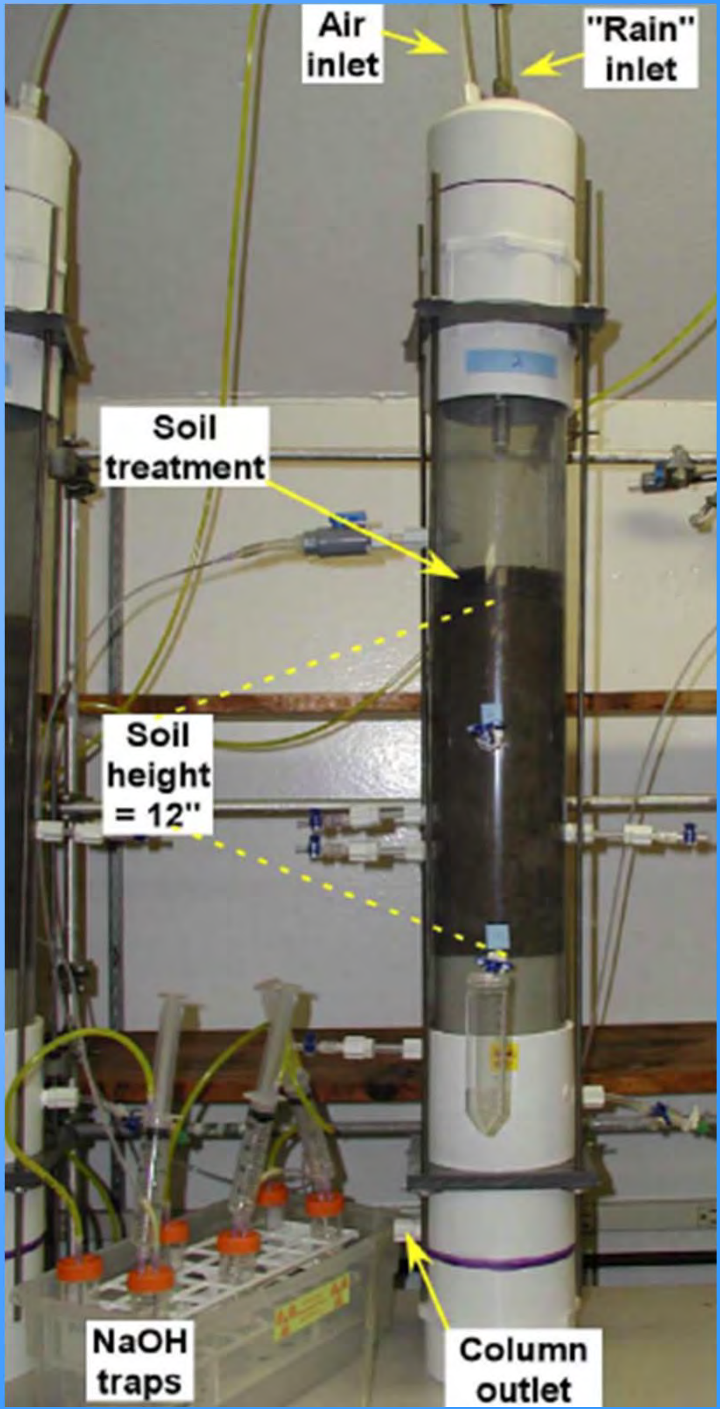
Fuller et al. (CU-1229)

- Add organic carbon to soil surface to enhance sorption / biodegradation



Fuller et al. (CU-1229)

- **Unsaturated soil columns**
  - 12 inch MMR soil
  - 0.5 inch surface treatment
- **Treatments**
  - Control
  - Peat
  - Peat + soybean oil
- **At 4 inch (10 cm) below surface**
  - TNT reduced by 100%
  - RDX reduced by 60%
  - HMX reduced by 40%
- **Similar results in larger scale field pilot test**



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Surface Treatment with Peat+Soybean Oil

- Operational Issues
  - Dust
  - Fire
  - How to distribute on active ranges
  - Disturbance by ordinance detonation

- Moderately effective
  - May not generate fully anaerobic condition

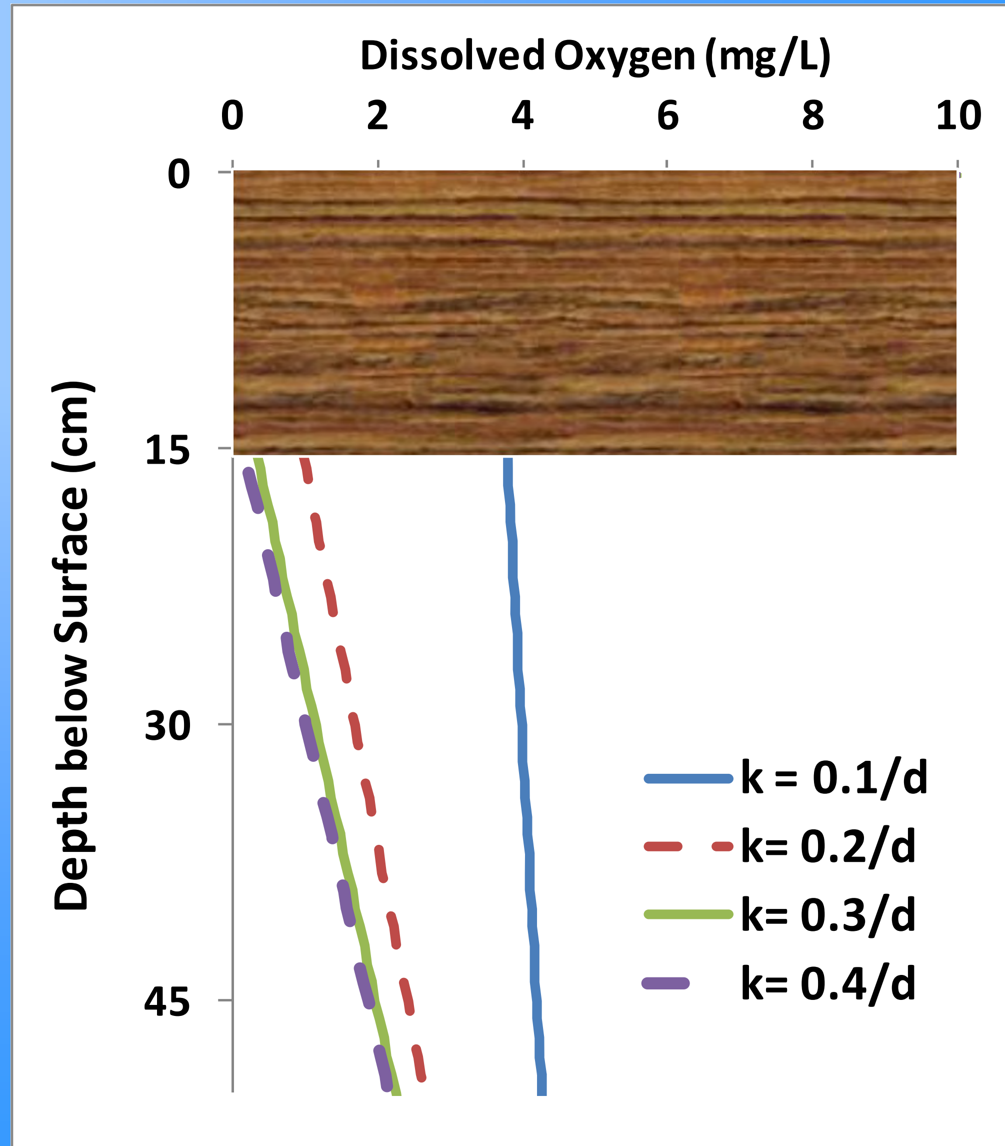
Oxygen Consumption with Added Organic Substrate

- **Objective:**
  Determine degradation rate and substrate thickness needed to reduce $O_2 < 0.1$ mg/L

- **Oxygen Transport Model**
  - O_2 diffuses through air filled pores in sand
  - O_2 consumed by substrate

$$\frac{dO}{dt} = -k\left(\frac{O}{O+K_O}\right)\left(\frac{S}{S+K_S}\right)$$

Substrate 15 cm (6 inch) thick



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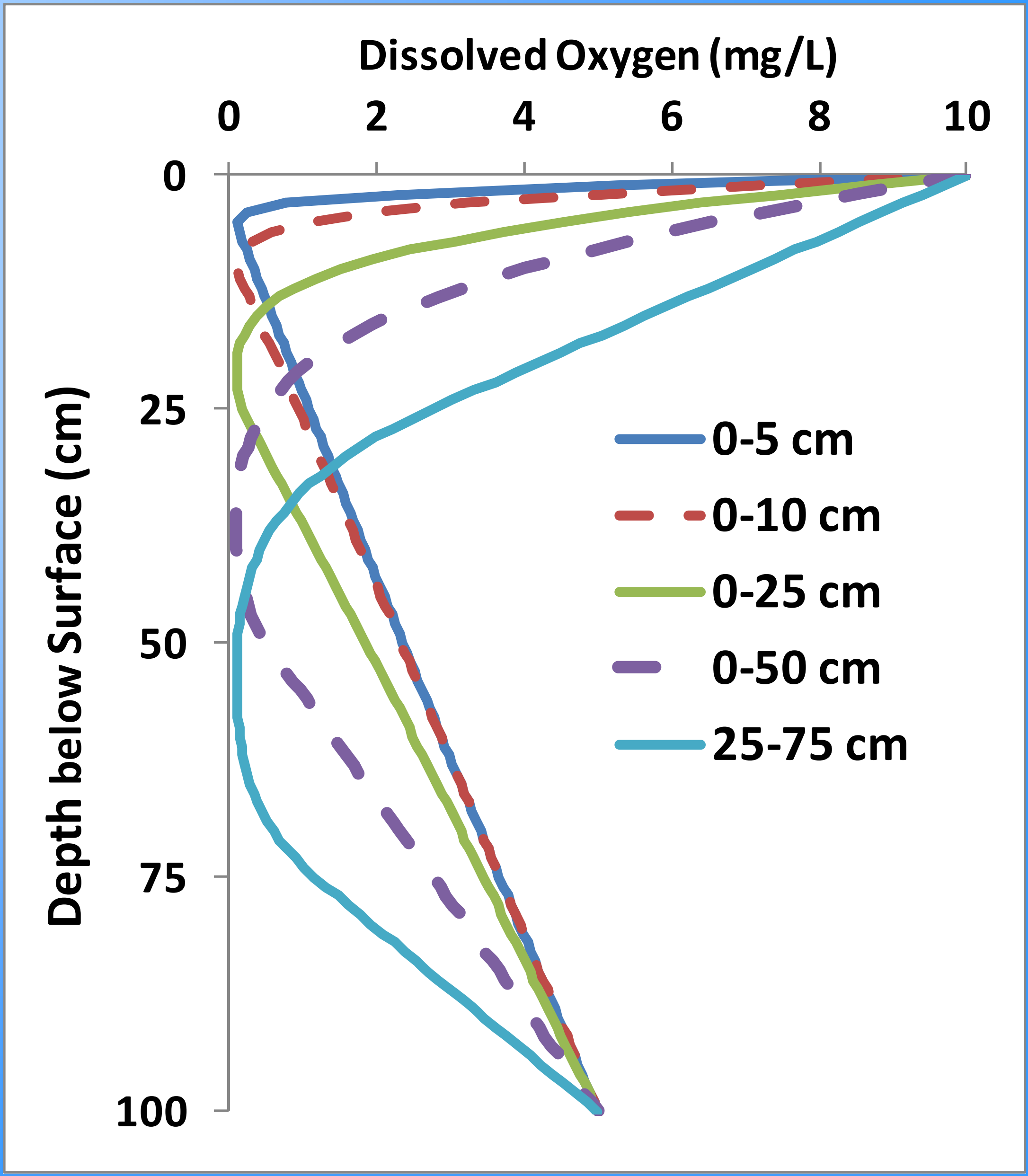
Oxygen Consumption with Added Organic Substrate

- **Objective:**
  Evaluate effect of substrate thickness on oxygen profile

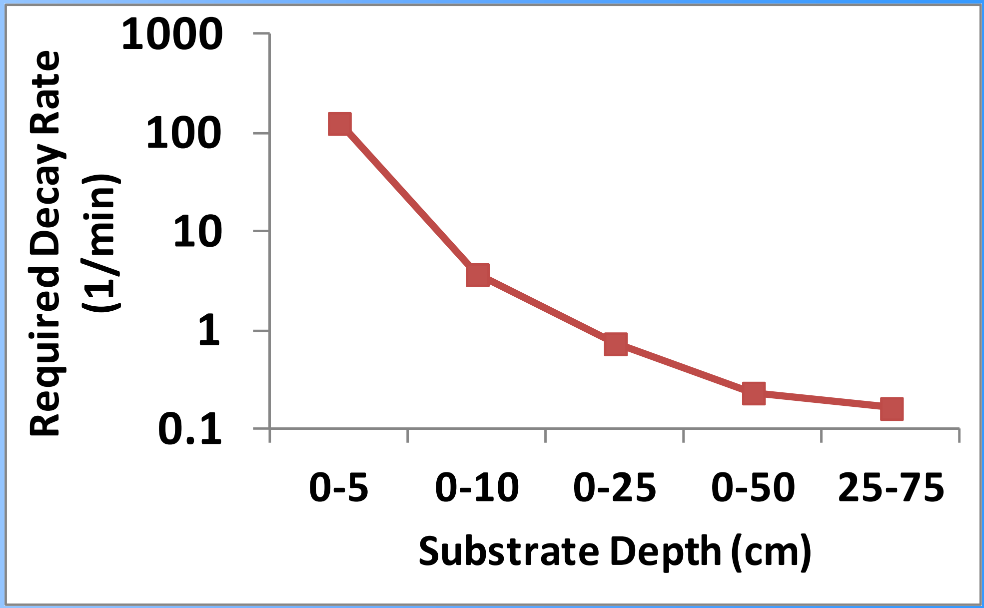
- **Layer thickness**
  - 5 cm (2 inch)
  - 10 cm (4 inch)
  - 25 cm (10 inch)
  - 50 cm (20 inch)

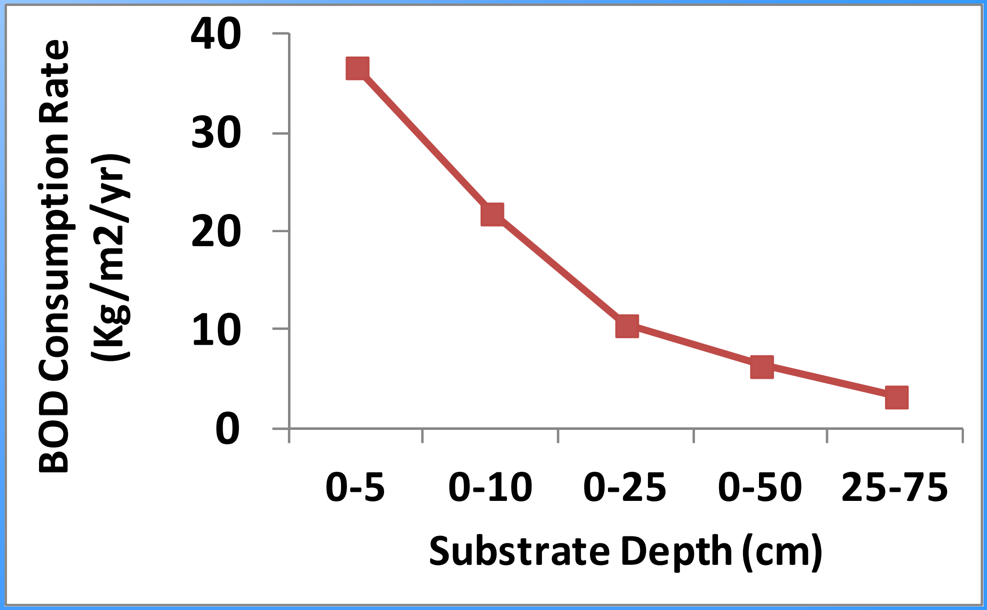
- **Adjust k so $O_2 < 0.1$ mg/L**



Oxygen Consumption Model Results

- **Thin Surface Layer**
  - Rapid oxygen transport
  - Very rapid biodegradation required to reduce O_2<0.01 mg/L
  - Rapid substrate consumption
- **Thick Surface Layer**
  - Required biodegradation rate is lower
  - Substrate lasts longer
- **Buried Substrate**
  - Reduces oxygen penetration
  - Lowest substrate consumption





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Substrate Application Method

- Surface Layer
  - Advantage – Easy to Apply
  - Disadvantages
    - Rapid oxygen penetration
    - Rapid biodegradation
    - Frequent application required
    - Fire, dust, disturbance by ordinance
- Deep Burial
  - Distribution is much more difficult
  - Extensive UXO clearance required

ER - 201123: In Situ Formation of biodegradation/sorption barriers

- Spray apply
  - Soluble organic substrate
    - Generates anaerobic conditions
    - Degrades contaminants, increases Fe(II) content
  - Soluble humics
    - Increases metals and explosives sorption / contact time
    - Consumes oxygen
    - Potentially serve as electron shuttles
- Irrigate
  - Transports amendments into soil
  - Generate more strongly reducing conditions
  - Increase longevity

Technical Requirements

- Process enhances contaminant degradation
- Protect groundwater
- Amendments
  - Low cost
  - Long-lasting
  - Non-toxic
- Spray apply
  - No tilling required
  - Limited entry onto range (UXO hazards)
- No secondary impacts (dust / stormwater / fire)

Soluble Substrate

- **Crude Glycerol**
  - **Byproduct of biodiesel production (0.1 Kg / Kg biodiesel)**
  - **Chemical Oxygen Demand = 1.1 g/g**
  - **Soluble, easy to infiltrate**
  - **Cheap, easily available**
- **Rapidly Biodegrades**
  - **Glycerol consumes oxygen**
  - **Degrades contaminants already present in soil**
  - **Reduces $Fe(OH)_3 \rightarrow Fe^{+2}$**

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Humic Material

- Required characteristics
  - Transported into soil
  - Sorb/bind/precipitate in place
  - No fire hazards
  - Low cost
- Potential Materials
  - Soluble humates
  - Lignosulfonate dust suppressants (liquid and powder)
  - Kraft lignin with alkali (NaOH or $Ca(OH)_2$)
  - Partially sulfonated Kraft lignin

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Fire Hazard?

Day 0
Sand treated with
Glycerol and Lignin

Day 3
After watering (2 inches)
Trying to burn sand

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Technical Approach

- Task 1: Laboratory Studies
  - Humic Material Selection
  - In Situ Treatment of Existing Contamination
  - Prevention of Future Leaching
- Task 2: Medium Scale Field-Pilot Tests
- Task 3: Field Demonstration
- Task 4: Documentation

Humic Material Selection

Type	Humic Material	Carbon	Water Saturation
Control	--	--	32%
Ligno-sulfonate	Norlig A	40%	28%
	Ultrazine	45%	**35%**
	Borresperse	43%	31%
Humate	Dry Soluble 80	32%	33%
	Organo Liquid Hume	37%	**38%**
	BorreGro HA-1	30%	31%
	BorreGro HA-2	40%	35%
Kraft Lignin	REAX 85A	49%	**37%**
	Indulin AT	62%	**37%**

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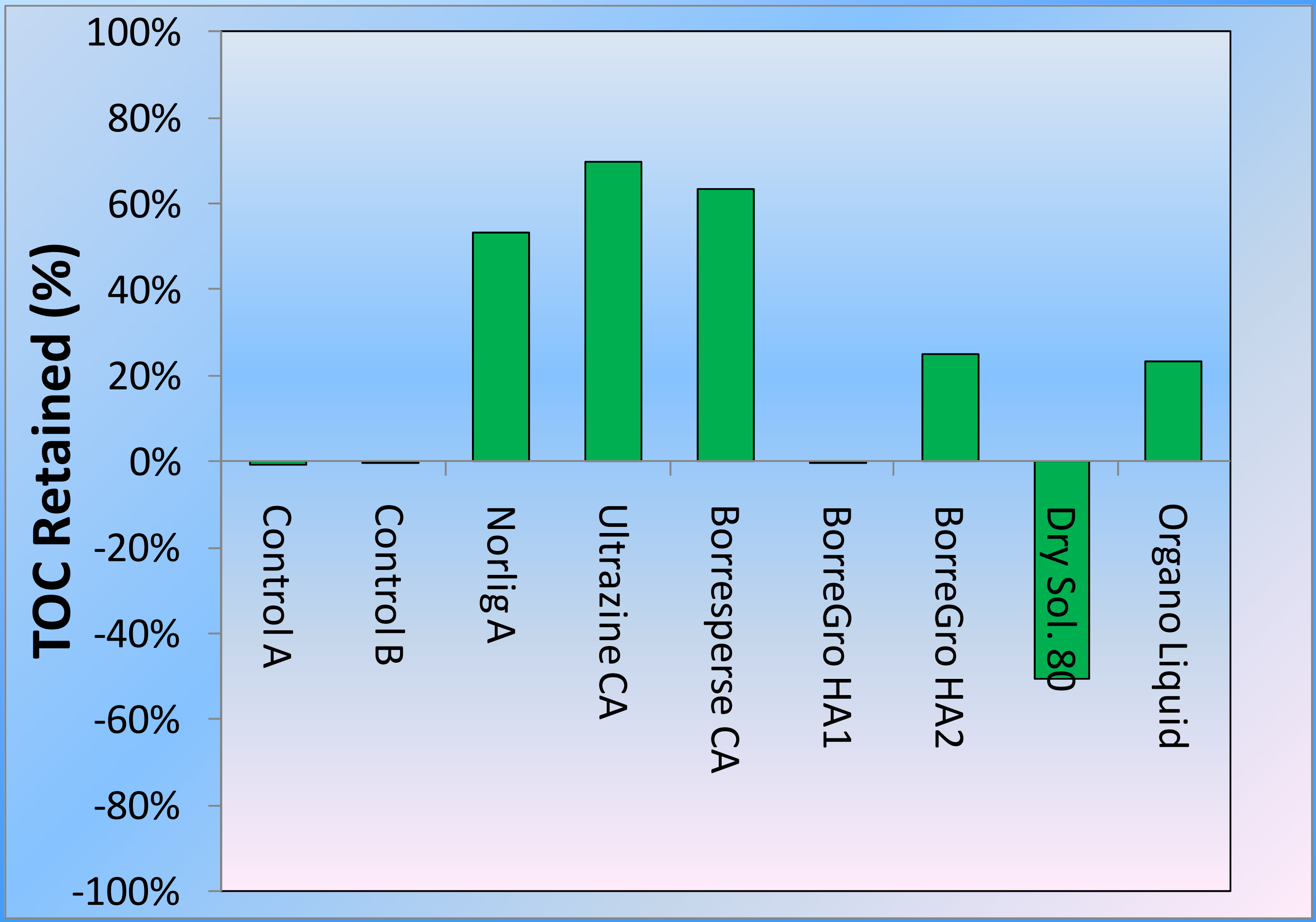
Humic Leaching Experiments

- 1 cm water, every other day
- Sacrifice columns after 3 months



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Lab Column Studies

- **Treatments:**
  - **Glycerol only**
  - **Kraft Lignin**
  - **Lignosulfonate**
  - **Glycerol + Kraft Lignin**
  - **Glycerol + Lignosulfonate**
  - **Untreated control**
- **Monitoring**
  - **Contaminants - RDX, HMX, TNT, ClO_4, degradation products**
  - **Indicator parameters - TOC, UV absorbance, pH, NO_3, Fe and SO_4**
  - **Soil gas -- N_2, O_2, CO_2 and CH_4**
  - **Extract soils at end of experiment**

Gas sampling ports

Effluent sampling

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Expected Benefits

- Develop alternative approach to treat / manage munitions impacted soils
- Complements other BMPs
- Applicable to variety of sites
  - Already contaminated soils
  - Where UXO has not yet been cleared.
  - Disturbed topography (craters)
  - Acidic soils with significant clay / iron hydroxides
  - Vegetated sites
  - Spot treatment of ranges after ordinance clearance